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**Synthesis of Bis(8-aminoquinoline)-substituted Tetraazacrown
Ethers by a Reductive Amination Process**

by

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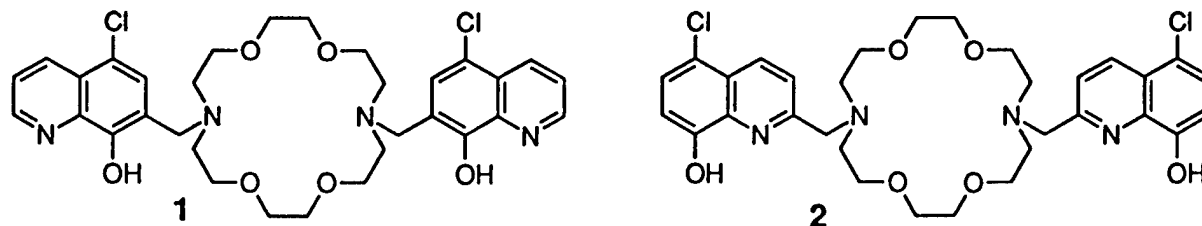
SYNTHESIS OF BIS(8-AMINOQUINOLINE)-SUBSTITUTED
TETRAAZACROWN ETHERS BY A REDUCTIVE AMINATION PROCESS

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Results and Discussion

Synthesis of Quinoline Derivative-containing Tetraazacrown Ethers. We have reported two methods of attaching 5-chloro-8-hydroxyquinoline to diaza-18-crown-6 (to form 1 and 2).¹ Ligand 2 was prepared by a nucleophilic substitution of the secondary nitrogens on the macrocycle ring on halomethyl-substituted 8-methoxyquinoline followed by removal of the methyl groups.¹ Ligand 1 was prepared by conversion of the secondary amines of the macrocycle to (methoxymethyl)amines which are active electrophilic reagents in the Mannich reaction and react readily with the electron rich phenolic side of 5-chloro-8-hydroxyquinoline.¹ We attempted to prepare the quinoline derivative-containing tetraaza macrocycles by these two



Reactions of aldehydes with primary or secondary amines in the presence of reducing agents to give secondary or tertiary amines, respectively, known as reductive amination, are useful methods to alkylate amine groups. Direct reductive amination of aldehydes with amines using sodium triacetoxyborohydride ($\text{NaBH}(\text{OAc})_3$) as a reducing agent has been developed for a wide variety of substrates.² Compared to other hydride reducing agents such as sodium cyanoborohydride (NaBH_3CN), $\text{NaBH}(\text{OAc})_3$ is mild, less toxic and exhibits remarkable selectivity as a reducing agent.²

To investigate the feasibility of synthesizing the quinoline derivative-containing tetraazamacrocycles by reductive amination, macrocycle 3 (see our Technical Report No. 4) was treated with 2-pyridinecarbaldehyde and 2-quinolinecarboxaldehyde in the presence of

NaBH(OAc)₃ to form pyridine- and quinoline-substituted tetraaza-15-crown-5 ligands **4** and **5** in 87% and 82% yields, respectively (Scheme 1). Although NaBH(OAc)₃ is a very mild reducing agent, a small amount of alcohol reduction product from the aldehyde was observed.

In the complex of CHQ-containing **2** with Ba²⁺, the cation is coordinated by all nitrogen and oxygen atoms of the ligand.³ To compare the effect of the hydroxy oxygen atom of 8-hydroxyquinoline in metal ion complexation with that of an amine nitrogen atom, a series of macrocycles containing 8-aminoquinoline side arms was also prepared (see Scheme 2). 8-Nitroquinolin-2-carbaldehyde was reacted with the NH functions on tetraazacrown ethers **3** and **6-8** by reductive amination to form 8-nitroquinoline-containing compounds **9-12**. Even though an excess amount of 8-nitroquinoline-2-carbaldehyde was used, some mono-substituted products were obtained. Decomposition of the 8-nitroquinoline-substituted compounds was observed within a couple of days so the nitro macrocycles were reduced immediately after purification. The nitro groups of compounds **9** and **10** were reduced by catalytic hydrogenation using platinum oxide as the catalyst to form **13** and **14** in 52% and 63% yields, respectively. Reduction of **11** and **12** was achieved using iron and HCl to form **15** and **16** in low yields. Decomposition of starting **11** and **12** was observed under this condition.

Experimental Section

The ¹H and ¹³C NMR spectra were recorded at 200 or 300 MHz and 50 or 75 MHz in CDCl₃ unless otherwise noted. MS spectra were determined using chemical ionization (CI) and fast atom bombardment (FAB) methods. All starting materials were either purchased from commercial sources or synthesized by known methods: 8-nitroquinolin-2-carbaldehyde⁴ and

tetraazacrown ethers **3**, **6-8**.⁵

General Procedure A: Reductive Amination of Pyridine- or Quinolinecarboxaldehyde with Tetraazacrown Ethers (Scheme 1). A mixture of the pyridine- or quinolinecarboxaldehyde and the macrocyclic diamine in $\text{ClCH}_2\text{CH}_2\text{Cl}$ was stirred with 1.3-1.6 equiv of $\text{NaBH}(\text{OAc})_3$ under a N_2 atmosphere at rt. The reaction was monitored by TLC. When the reaction was completed, 1*N* HCl was added to terminate the reaction. Then 1*N* NaOH was added to adjust the pH value of the solution to pH 10-12. The solution was then extracted several times by portions of CH_2Cl_2 . The combined CH_2Cl_2 extracts were dried (Na_2SO_4), filtered, and evaporated to give the crude product. The crude product was purified by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{NH}_4\text{OH}$) to give the product.

7,13-Bis((2-pyridinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-oxacyclopentadecane (4) (Scheme 1). Compound **4** (185 mg, 87%) was obtained as an oil according to general procedure A from 2-pyridinecarboxaldehyde (110 mg, 1 mmol) and **3** (122 mg, 0.5 mmol); ^1H NMR δ 8.49 (d, $J = 7.1$ Hz, 2H), 7.63 (t, $J = 6.8$ Hz, 2H), 7.54 (d, $J = 7.1$ Hz, 2H), 7.13 (t, $J = 6.8$ Hz, 2H), 3.79 (s, 4H), 3.52 (t, $J = 6.1$ Hz, 4H), 2.83-2.77 (m, 8H), 2.62-2.56 (m, 8H), 2.22 (s, 6H); ^{13}C NMR δ 160.3, 149.1, 136.5, 123.3, 122.0, 70.5, 61.6, 55.4, 55.2, 54.2, 53.0, 44.5; MS (FAB) m/z 449 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{24}\text{H}_{39}\text{N}_6\text{O}$ (MH^+): 427.3185, found: 427.3181.

7,13-Bis((2-quinolinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-oxacyclopentadecane (5) (Scheme 1). Compound **5** (216 mg, 82%) was obtained as an oil according to general procedure A from 2-quinolinecarboxaldehyde (157 mg, 1 mmol) and **3** (122 mg, 0.5 mmol); ^1H NMR δ 8.03 (d, $J = 8.3$ Hz, 2H), 7.93 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 7.8$ Hz, 2H), 7.54-7.51 (m, 4H), 7.41-7.36 (m, 2H), 3.84 (s, 4H), 3.40-3.35 (m, 4H), 2.86-2.71 (m,

16H), 2.38 (s, 6H); ^{13}C NMR δ 160.3, 147.5, 136.6, 129.5, 128.8, 127.6, 127.3, 126.2, 121.2, 69.7, 61.7, 54.7, 54.4, 53.2, 51.8, 43.0; MS (FAB) m/z 549 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{32}\text{H}_{43}\text{N}_6\text{O}$ (MH^+): 527.3498, found: 527.3506; Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{N}_6\text{O}$: C, 72.97; H, 8.04. Found: C, 72.74, H, 8.18.

7,13-Bis((8-nitro-2-quinolinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-oxacyclopentadecane (9) (Scheme 2). Compound 9 (169 mg, 55%) was obtained as an oil according to general procedure A from 3 (122 mg, 0.5 mmol) and 8-nitroquinolin-2-carboxaldehyde (274 mg, 1.4 mmol); ^1H NMR δ 8.20 (d, $J = 8.7$ Hz, 2H), 7.99 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.96 (dd, $J = 7.6, 1.2$ Hz, 2H), 7.89 (d, $J = 8.7$ Hz, 2H), 7.55 (dd, $J = 7.6, 8.3$ Hz, 2H), 4.00 (s, 4H), 3.51 (t, $J = 4.8$ Hz, 4H), 2.91 (t, $J = 6.6$ Hz, 4H), 2.82 (t, $J = 4.8$ Hz, 4H), 2.71-2.66 (m, 8H), 2.28 (s, 6H); ^{13}C NMR δ 164.1, 148.3, 138.9, 136.2, 131.7, 128.3, 124.8, 123.3, 123.2, 70.2, 61.7, 55.3, 54.9, 54.5, 52.9, 44.2; MS (FAB) m/z 639 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{32}\text{H}_{41}\text{N}_8\text{O}_5$ (MH^+): 617.3199, found: 617.3211.

8,14-Bis((8-nitro-2-quinolinyl)methyl)-1,5-dimethyl-1,5,8,14-tetraaza-11-oxacyclohexadecane (10) (Scheme 2). Compound 10 (164 mg, 52%) was obtained as an oil according to general procedure A from 6 (129 mg, 0.5 mmol) and 8-nitroquinolin-2-carboxaldehyde (274 mg, 1.4 mmol); ^1H NMR δ 8.19 (d, $J = 8.6$ Hz, 2H), 7.99 (dd, $J = 8.3, 1.2$ Hz, 2H), 7.96 (dd, $J = 7.6, 1.2$ Hz, 2H), 7.89 (d, $J = 8.6$ Hz, 2H), 7.55 (dd, $J = 7.6, 8.3$ Hz, 2H), 3.99 (s, 4H), 3.53 (t, $J = 4.9$ Hz, 4H), 2.90-2.78 (m, 8H), 2.60 (t, $J = 6.6$ Hz, 4H), 2.53 (t, $J = 6.8$ Hz, 4H), 2.23 (s, 6H), 1.69 (p, $J = 6.6$ Hz, 2H); ^{13}C NMR δ 164.3, 148.3, 138.9, 136.2, 131.7, 128.3, 124.7, 123.3, 123.2, 69.9, 61.6, 55.9, 55.1, 54.4, 52.7, 43.3, 24.9; MS (FAB) m/z 631 (MH^+), 653 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_8\text{O}_5$ (MH^+): 631.3356, found: 631.3353.

7,13-Bis((8-nitro-2-quinolinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-thiacyclo-

pentadecane (11) (Scheme 2). Compound **11** (200 mg, 63%) was obtained as an oil according to general procedure A from **7** (130 mg, 0.5 mmol) and 8-nitroquinolin-2-carboxaldehyde (274 mg, 1.4 mmol); ^1H NMR δ 8.18 (d, J = 8.7 Hz, 2H), 7.97 (dd, J = 8.1, 1.5 Hz, 2H), 7.94 (dd, J = 7.8, 1.5 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.53 (dd, J = 7.8, 8.1 Hz, 2H), 3.97 (s, 4H), 2.89-2.79 (m, 4H), 2.76-2.68 (m, 8H), 2.64-2.58 (m, 8H), 2.22 (s, 6H); ^{13}C NMR δ 163.8, 148.3, 138.9, 136.2, 131.6, 128.3, 124.8, 123.3, 123.0, 61.6, 55.8, 55.6, 54.9, 51.9, 43.5, 29.7; MS (FAB) m/z 633 (MH^+), 655 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{32}\text{H}_{40}\text{N}_8\text{O}_4\text{Na}$ (MNa^+): 655.2791, found 655.2797.

8,14-Bis((8-nitro-2-quinolinyl)methyl)-1,5-dimethyl-1,5,8,14-tetraaza-11-thiacyclohexadecane (12) (Scheme 2). Compound **12** (165 mg, 51%) was obtained as an oil according to general procedure A from **8** (137 mg, 0.5 mmol) and 8-nitroquinolin-2-carboxaldehyde (274 mg, 1.4 mmol); ^1H NMR δ 8.19 (d, J = 8.6 Hz, 2H), 7.99 (dd, J = 8.3, 1.2 Hz, 2H), 7.96 (dd, J = 8.3, 1.2 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.55 (dd, J = 7.8, 8.2 Hz, 2H), 3.99 (s, 4H), 2.90-2.85 (m, 4H), 2.78-2.68 (m, 8H), 2.56 (t, J = 6.6 Hz, 4H), 2.49 (t, J = 7.0 Hz, 4H), 2.19 (s, 6H), 1.69 (p, J = 7.0 Hz, 2H); ^{13}C NMR δ 164.0, 148.3, 138.9, 136.2, 131.7, 128.3, 124.8, 123.4, 123.0, 61.5, 55.6, 55.4, 54.9, 52.1, 43.4, 30.0, 25.3; MS (FAB) m/z 647 (MH^+), 669 (MNa^+); HRMS (FAB) Calcd for $\text{C}_{33}\text{H}_{43}\text{N}_8\text{O}_4\text{S}$ (MH^+): 647.3128, found: 647.3122.

General Procedure B: Catalytic Hydrogenation of Nitroquinoline Substituted Macrocycles. To a solution of 8-nitro-2-quinolinylmethyl-substituted macrocycle in 100 mL of MeOH in a 500 mL pressure vessel was added 0.3 g of PtO_2 (Adam's catalyst). The head and fittings were attached and the vessel was connected to a H_2 cylinder. The system was alternately evacuated and pressurized with H_2 to 40-50 psi three times. After a final evacuation, H_2 was introduced into the vessel until the pressure reached 100 psi. The reaction was allowed to

proceed overnight. The vessel was vented, the catalyst was removed by filtration and the reaction mixture was washed with MeOH. The filtrates are combined and the solvent was removed under reduced pressure to give an yellow oil. The product was purified by chromatography on silica gel (40:5:1/CH₂Cl₂:MeOH:NH₄OH).

7,13-Bis((8-amino-2-quinolinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-oxacyclopentadecane (13) (Scheme 2). Compound 13 (130 mg, 88%) was obtained as an oil according to general procedure B from 9 (160 mg, 0.26 mmol); ¹H NMR δ 8.00 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 7.26 (dd, *J* = 8.3, 7.6 Hz, 2H), 7.12 (dd, *J* = 8.3, 1.2 Hz, 2H), 6.91 (dd, *J* = 7.6, 1.2 Hz, 2H), 5.00 (br s, 4H), 3.95 (s, 4H), 3.53 (t, *J* = 4.6 Hz, 4H), 2.93 (t, *J* = 6.4 Hz, 4H), 2.70 (m, 12H), 2.31 (s, 6H); ¹³C NMR δ 143.9, 137.7, 136.4, 127.9, 127.0, 121.8, 116.0, 110.3, 70.4, 62.0, 55.4, 54.7, 54.2, 52.7, 44.1; MS (FAB) *m/z* 579 (MNa⁺); HRMS (FAB) Calcd for C₃₂H₄₅N₈O (MH⁺): 557.3716, found: 557.3715. Anal. Calcd for C₃₂H₄₄N₈O·1HCl·1.5H₂O: C, 61.97; H, 7.80. Found: C, 62.09; H, 7.45.

8,14-Bis((8-amino-2-quinolinyl)methyl)-1,5-dimethyl-1,5,8,14-tetraaza-11-oxacyclohexadecane (14) (Scheme 2). Compound 14 (106 mg, 81%) was obtained as an oil according to general procedure B from 10 (145 mg, 0.23 mmol); ¹H NMR δ 7.99 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.28 (dd, *J* = 8.1, 7.6 Hz, 2H), 7.11 (d, *J* = 8.1, Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 4.97 (s, 4H), 3.95 (s, 4H), 3.56 (t, *J* = 5.1 Hz, 4H), 2.89-2.82 (m, 8H), 2.60 (t, *J* = 6.8 Hz, 4H), 2.49 (t, *J* = 6.8 Hz, 4H), 2.21 (s, 6H), 1.65 (p, *J* = 6.6 H, 2H); ¹³C NMR δ 158.1, 143.8, 137.6, 136.3, 127.9, 126.9, 121.7, 116.0, 110.2, 70.2, 62.0, 56.1, 55.4, 54.1, 52.9, 43.5, 25.3; MS (FAB) *m/z* 571 (MH⁺), 593 (MNa⁺); HRMS (FAB) Calcd for C₃₃H₄₇N₈O (MH⁺): 571.3873, found: 571.3857. Anal. Calcd for C₃₃H₄₆N₈O: C, 69.44; H, 8.12. Found: C, 69.26; H, 7.94.

General Procedure C: Reduction of Nitroquinoline-substituted Macrocycles by

Reduced Iron and Hydrochloric Acid. A mixture of 8-nitro-2-quinolinylmethyl-substituted macrocycle, reduced Fe (400 mg), 5 mL of 95% EtOH, 1 mL of water and 0.1 mL of concentrated HCl was refluxed for 1 h. The Fe was removed by filtration and washed with portions of hot 95% EtOH. The filtrate and washings were evaporated. The residue was dissolved in CH₂Cl₂ and washed with aqueous Na₂CO₃. The organic layer was separated and dried (Na₂SO₄). The crude product was purified by chromatography on silica gel (40:5:1/CH₂Cl₂:MeOH:NH₄OH).

7,13-Bis((8-amino-2-quinolinyl)methyl)-1,4-dimethyl-1,4,7,13-tetraaza-10-thiacyclohexadecane (15) (Scheme 2). Compound 15 (43 mg, 36%) was obtained as an oil according to general procedure C from 11 (130 mg, 0.21 mmol); ¹H NMR δ 8.00 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.30 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.92 (d, 7.3 Hz, 2H), 4.97 (br s, 4H), 3.94 (s, 4H), 2.93-2.88 (m, 4H), 2.78-2.70 m, 8H), 2.63-2.56 (m, 8H), 2.21 (s, 6H); ¹³C NMR δ 157.7, 143.9, 137.7, 136.4, 128.0, 127.0, 121.6, 116.1, 110.3, 62.1, 56.0, 55.0, 52.3, 43.6, 29.4; MS (FAB) *m/z* 595 (MNa⁺); HRMS (FAB) Calcd for C₃₂H₄₄N₈SNa (MNa⁺): 595.3307, found: 595.3310. Anal. Calcd for C₃₂H₄₄N₈S·1.5 HCl·0.5 H₂O: C, 60.38; H, 7.36. Found: C, 60.69; H, 7.10.

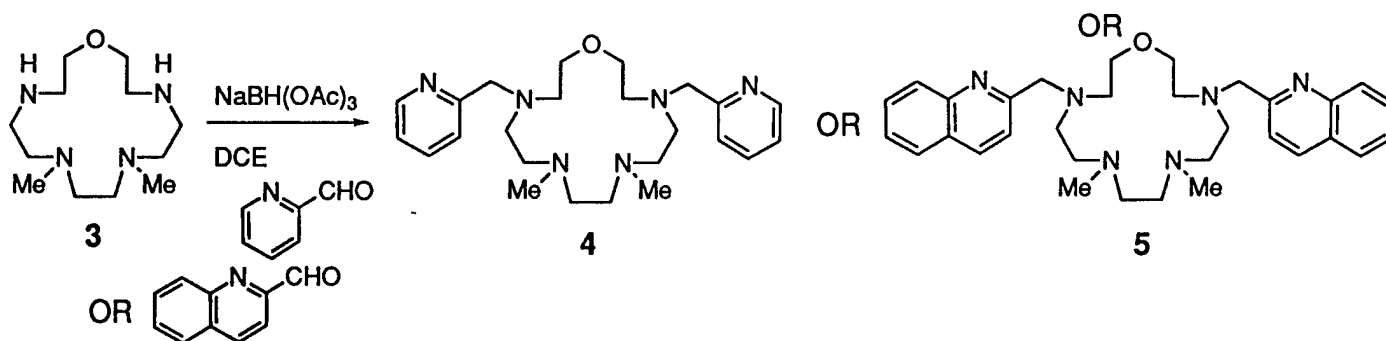
8,14-Bis((8-amino-2-quinolinyl)methyl)-1,5-dimethyl-1,5,8,14-tetraaza-11-thiacyclohexadecane (16) (Scheme 2). Compound 16 (41 mg, 33%) was obtained as an oil according to general procedure C from 12 (135 mg, 0.21 mmol); ¹H NMR δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.28 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.12 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.90 (dd, *J* = 7.3, 1.0 Hz, 2H), 4.96 (br s, 4H), 3.94 (s, 4H), 2.90-2.85 (m, 4H), 2.75-2.68 (m, 8H), 2.54 (t, *J* = 7.1 Hz, 4H), 2.46 (t, *J* = 7.1 Hz, 4H), 2.18 (s, 6H), 1.67 (p, *J* = 6.8 Hz, 2H); ¹³C NMR δ 157.7, 143.9, 137.6, 136.4, 128.0, 127.0, 121.6, 116.1, 110.3, 61.9, 55.7, 55.4, 54.9, 52.3, 43.5, 29.7,

25.5; MS (FAB) m/z 587 (MH^+), 609 (MNa^+); HRMS (FAB) Calcd for $C_{33}H_{47}N_8S$ (MH^+):

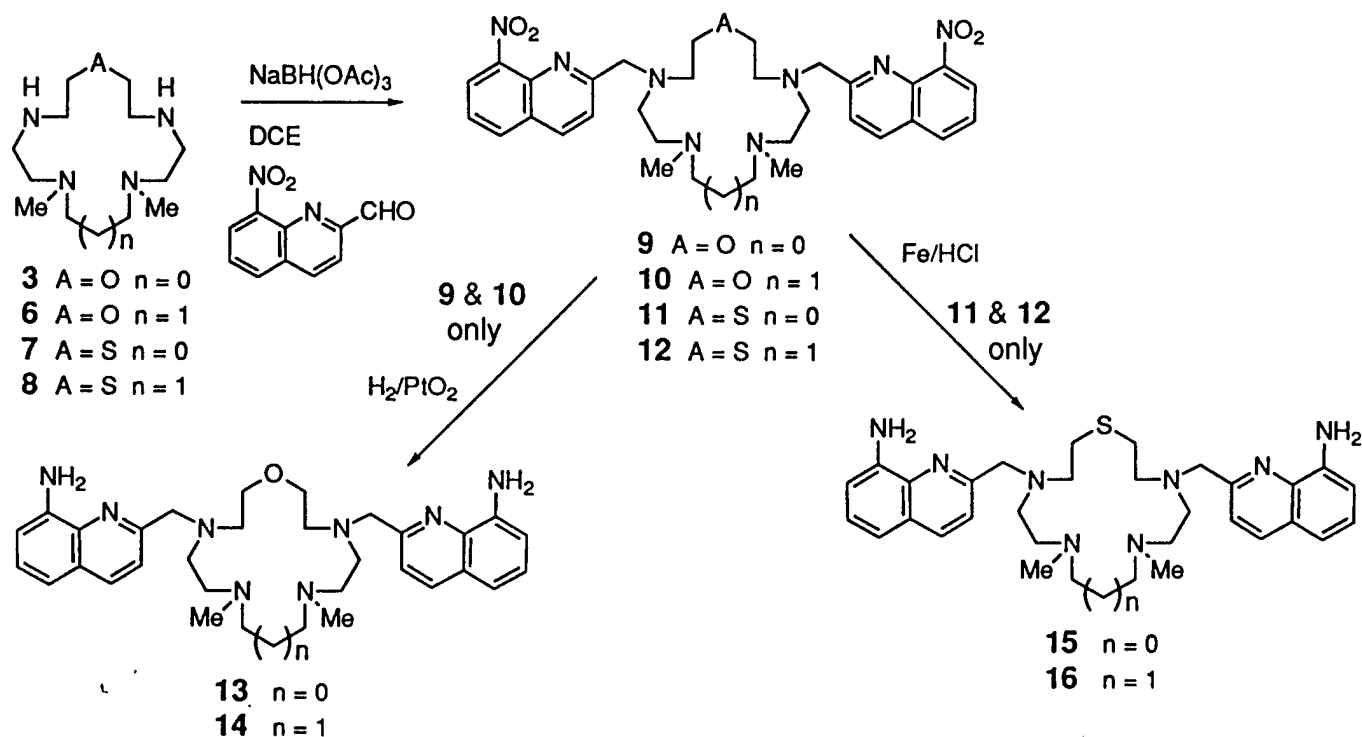
587.3644, found: 587.3638. Anal. Calcd for $C_{33}H_{46}N_8S \cdot 2HCl$: C, 60.08; H, 7.23. Found: C, 60.09; H, 6.86.

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Scheme 1. Syntheses of pyridine- and quinoline-substituted crown ethers via reductive amination



Scheme 2. Syntheses of 8-aminoquinoline-substituted tetraazacrown ethers